DIELS-ALDER ADDUCT ISOMERIZATION STUDIES USING DSC AND PMR METHODS

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ABSTRACT.

Model Diels-Alder (D-A) adducts of a different isomeric composition were synthesized using furfuryl acetate (FA) and maleimid (MI). The composition of synthesized isomers was analyzed using the proton-magnetic resonance method (PMR). The D-A adduct isomerization process was studied using the differential scanning calorimetry (DSC) method in the nonisothermal mode.

Keywords: Model Diels-Alder , Proton-magnetic resonance method, Adduct isomerization process, Differential scanning calorimetry method

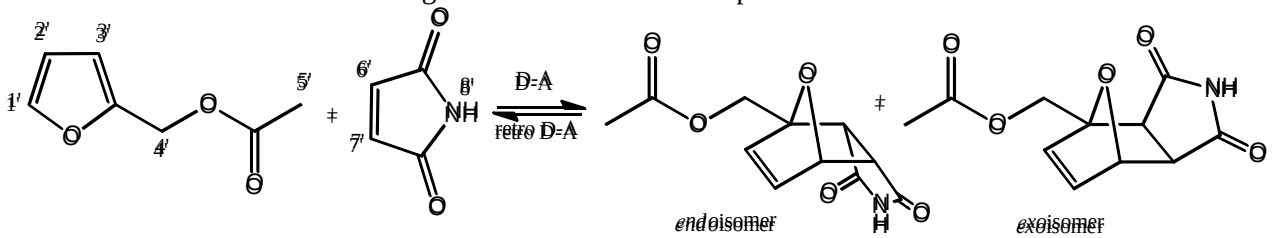
INTRODUCTION

The D-A adduct formation reaction is of great importance for the organic chemistry. A mild behavior of the D-A reaction and the possibility of the reverse reaction at an elevated temperature (the retrodiene reaction) are important and interesting factors of the chemical process. Over the last twenty years the polymers synthesized through the D-A reaction attracted great attention of scientists, because this approach gives an opportunity to produce thermally decomposable polymers of a different composition with different properties that can easily and repeatedly be reprocessed without degradation of their properties [1-5].

In our previous publications we described the synthesis of novel thermally decomposable "nonisocyanate" polyhydroxyurethanes based on the available renewable raw materials [6,7]. While studying kinematic parameters of the D-A adduct formation reaction using the DSC method in the nonisothermal mode we observed two thermal effects that were partially superimposed [7]. All similar reactions based on different maleimids or bismaleimids and furan-containing derivatives have specific DSC thermograms. The D-A reaction is a key reaction used for the production of thermally decomposable polymers that have linear and three-dimensional structures and therefore it requires in-depth studies of its mechanism.

This scientific paper delves into the investigation of the nature of thermal effects that are observed while studying the D-A reaction using the DSC method in the nonisothermal mode.

One of the well-known properties of D-A adducts is considered to be their isomerization, in particular the endoisomer- to-exoisomer conversion with an increase in temperature. Assumingly, this can be the reason for the appearance of the second thermal effect. To confirm or to abandon this hypothesis the isomerization process was studied using the model reaction of FA and MI. Particularly this diene and this dienophyl were selected for the investigation, because their PMR spectra allow for the efficient discrimination of the signals of individual isomer protons:



EXPERIMENT

Materials

Furfuryl alcohol (FA), carbamide, maleic anhydride (MA) and glacial acetic acid (AA) are commercial reagents bought from the "Laboratornyy Mir Ltd" Company. The content of the ground substance for all reagents is 99%. Prior to their use the FA and AA were distilled and the FA was subjected to drying over the calcium chloride.

Synthesis

The furfuryl acetate (FA) was synthesized using the acetylation reaction of the furfuryl alcohol with the acetic anhydride at 90°C during one hour. The reaction mixture was rinsed with the distilled water and the synthesized FA was distilled under the vacuum. The obtained FA is a clear liquid with a specific ether odour; $t_{boil.}$=(72–74)°C at 4 mm of mercury column; $n_d^{20}{}_{(theor.)}$=1.4410; $n_d^{20}{}_{(pract.)}$=1,4410. FA output makes up 92 mass % of the theoretical value. The PMR data (DMSO-d_6, δ (ppm)): 5'H(1.998)s; 4'H(5.015)s; 2',3'H(6.427-6.482)dd; 1'H(7.641)s (the proton notation is given in the above reaction).

The MI was synthesized using the technique [8]. The obtained MI is a crystalline substance of a white color with $t_{ml.}$= 92°C. The PMR data are as follows: (DMSO-d_6, δ (ppm)): 6',7'H(6.836)s; 8'H(10.832)s.

Experimental procedure

To determine the isomeric composition of the adducts during the studies of the D-A reaction using the DSC method all reactions were carried out in the DMSO-d_6 solution whose mass share made up 50% so as to analyze this reaction using the PMR-spectroscopy. All D-A reactions were studied in terms of equimolecular ratios of initial FA and MI.

The PMR spectroscopy was carried out using the Varion Mercury VX – 200 spectrophotometer and the DMSO-d_6 solvent.

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RESULTS AND DISCUSSION

It is possible to put forward several hypotheses as for the second thermal effect that was established while studying the D-A reaction using the DSC method to carry out the nonisothermal experiment. First, as it was mentioned above, it can be the isomerization process of D-A adducts. Secondly, we can assume that the retrodiene reaction follows the biradical mechanism or the ion-radical mechanism [9] as the temperature rises, which may in its turn result in the initiation of the radical polymerization of the free MI. To find an explanation for these assumptions the D-A reaction was blocked at a definite time (by the time of the origination of the second thermal effect (110ºC) and after it (140ºC) (Figure1) and the composition of the reaction mixture was investigated at these points using the PMR spectroscopy method (Figure 2).

In addition to two exothermal effects (the maximum temperature $T_{(max)}$ of the first effect is 85°C and the maximum temperature $T_{(max)}$ of the second effect is 117°C) the DSC thermogram shows the deviation of the scanning signal towards the endothermal effect at elevated temperatures (130ºC and higher). This is indicative of that the endothermal reaction (the D-A retrodiene reaction) occurs simultaneously with exothermal reactions (D-A adduct formation and the isomerization process)

A quantitative composition of isomers can be determined from the protons 1, 4, 6, 7 and 8. The analysis of PMR spectra (Figure 2) showed that the initial substances of the reaction mixture after the reaction suppression at 110ºC made up 42.5% and the isomeric composition of adducts (exo/endo) made up 72.3/27.7 %, respectively. After the reaction suppression at 140º C the initial substances of the reaction mixture made up 50% and the isomeric composition of the adducts (exo/endo) made up (73.8/26.2)%, respectively. Thus, the percentage of the exoisomer at the second test point is 1. 5% higher and the total quantity of adduct is reduced by 7. 5%, which is indicative of the occurrence of

the retrodiene D-A reaction. Probably, 1.5 % is an insignificant percentage to entirely assert that the isomerization is the reason of the second thermal effect. The amount of the free MI and FA is indicative of that the MI is not polymerized during the retrodiene reaction under these conditions.

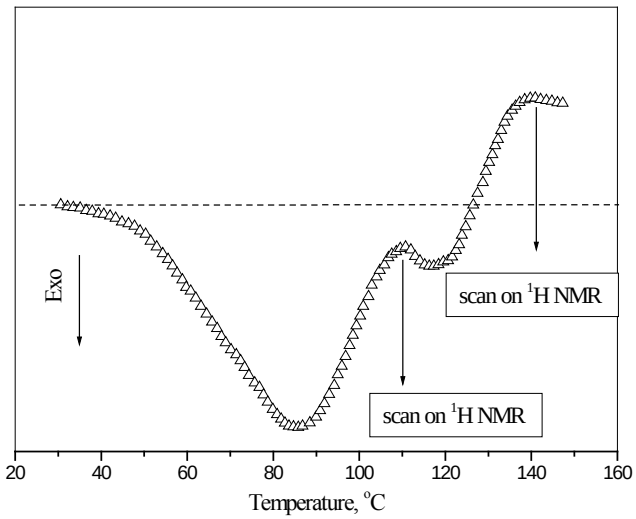

Figure 1. Thermal effect of the D-A adduct formation reaction that occurs between the FA and the MI

Since the above approach gave no clear results that would reveal the nature of the second thermal effect we decided to synthesize first D-A adducts of a different isomeric composition and then to study their conversion using the PMR spectroscopy and the DSC method (Fig.3 and Fig.4, accordingly). For this purpose the endoisomer was synthesized at 20ºC for 10 days and the exoisomer was synthesized at 90ºC for 10 hours using the method [10].

The analysis of PMR spectra (Figure 3) showed that the adducts that were synthesized at 20ºC (Figure 3.1) consisted of endo/exoisomers making up 68/32% respectively; the conversion of initial substances made up 91.1%.

Adducts that were synthesized at 90°C (Figure 3.2) consisted of endo/exoisomers (16/84) %, respectively and the conversion of initial substances was 90.2%. It can be seen that D-A adducts synthesized under such conditions differ significantly by their isomeric composition; the amount of endoisomer is 52% higher for the synthesis of adduct at a temperature of 20°C. The obtained D-A adducts (of a different isomer composition) were then studied using the DSC method (Figure 4).

The analysis data of the DSC- thermogram (Figure 4) allow us to assert that adducts with an ample quantity of exoisomers (Figure 4, curve 1) show only endothermal effect that sets in at 80º C and terminates at 130º C that is indicative of the retrodiene reaction. At a temperature of 130ºC and higher the exothermal effect develops, which applies to the polymerization of the decay products of D-A adducts.

For adducts with a large quantity of endoisomers (Figure 4, curve 24) the exothermal effect is clearly observed against the background of the endothermal reaction that starts at 60ºC and this exothermal effect develops at 100ºC and terminates at 140ºC, with $\boldsymbol{T}_{(max)}$ approaching 120 ºC. The amount of the released heat is equal to 8.8 kJ/mole. At a temperature of 140ºC and higher the subsequent exothermal effect sets in and it is related to the polymerization of the decay products of the D-A adduct. The temperature characteristics of the thermal effect, which is observed in the temperature range of 100 to 140ºC, strongly coincide with those of the second thermal effect (Figure 1). Only Figure4 shows its total manifestation and in Figure 1 it is partially overlapped by the first thermal effect.

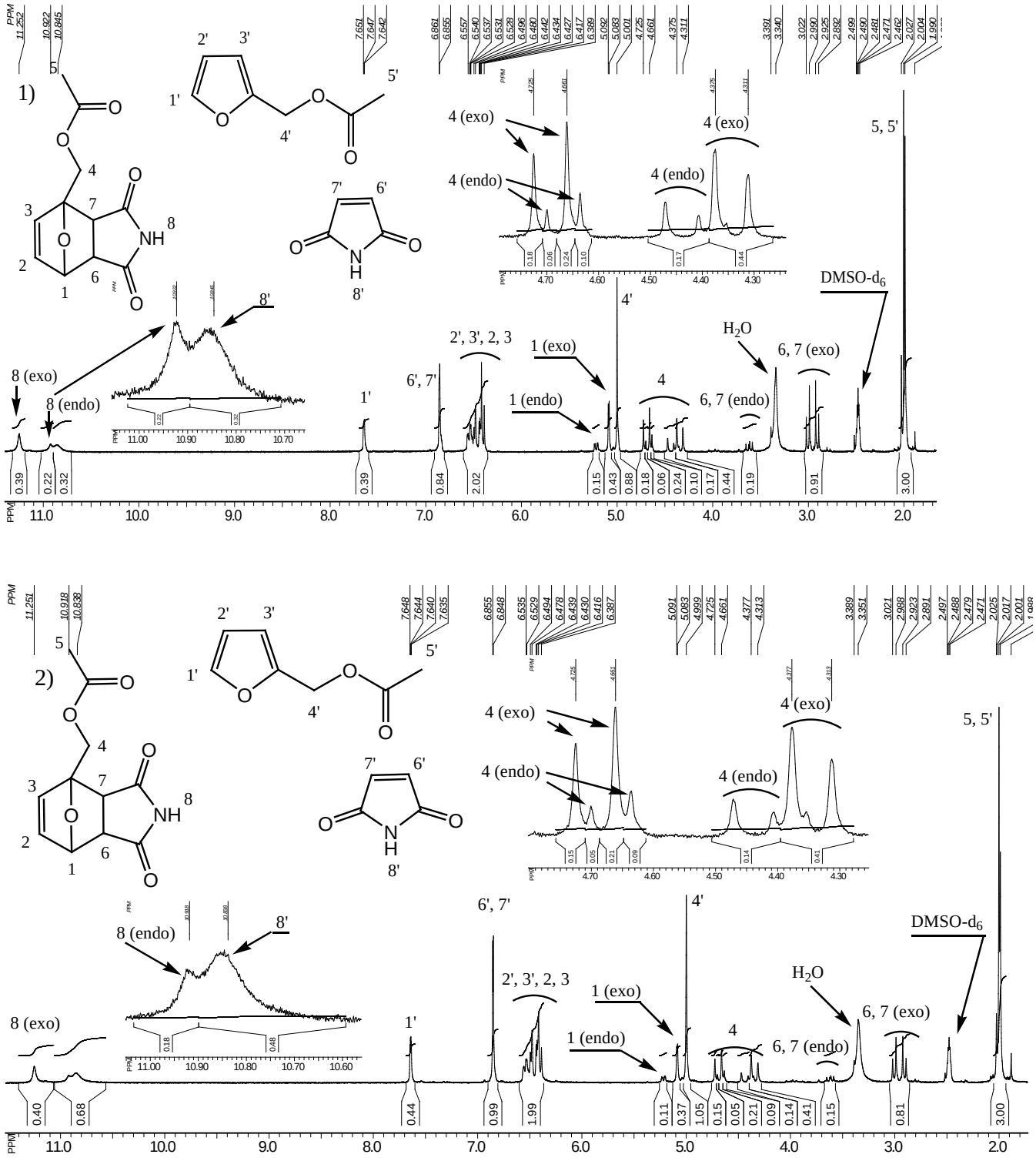

Figure 2. PMR spectra of the FA and MI reaction mixture of D-A adducts blocked during the DSC scanning: **1**) at 110 ºC; **2**) at 140ºC

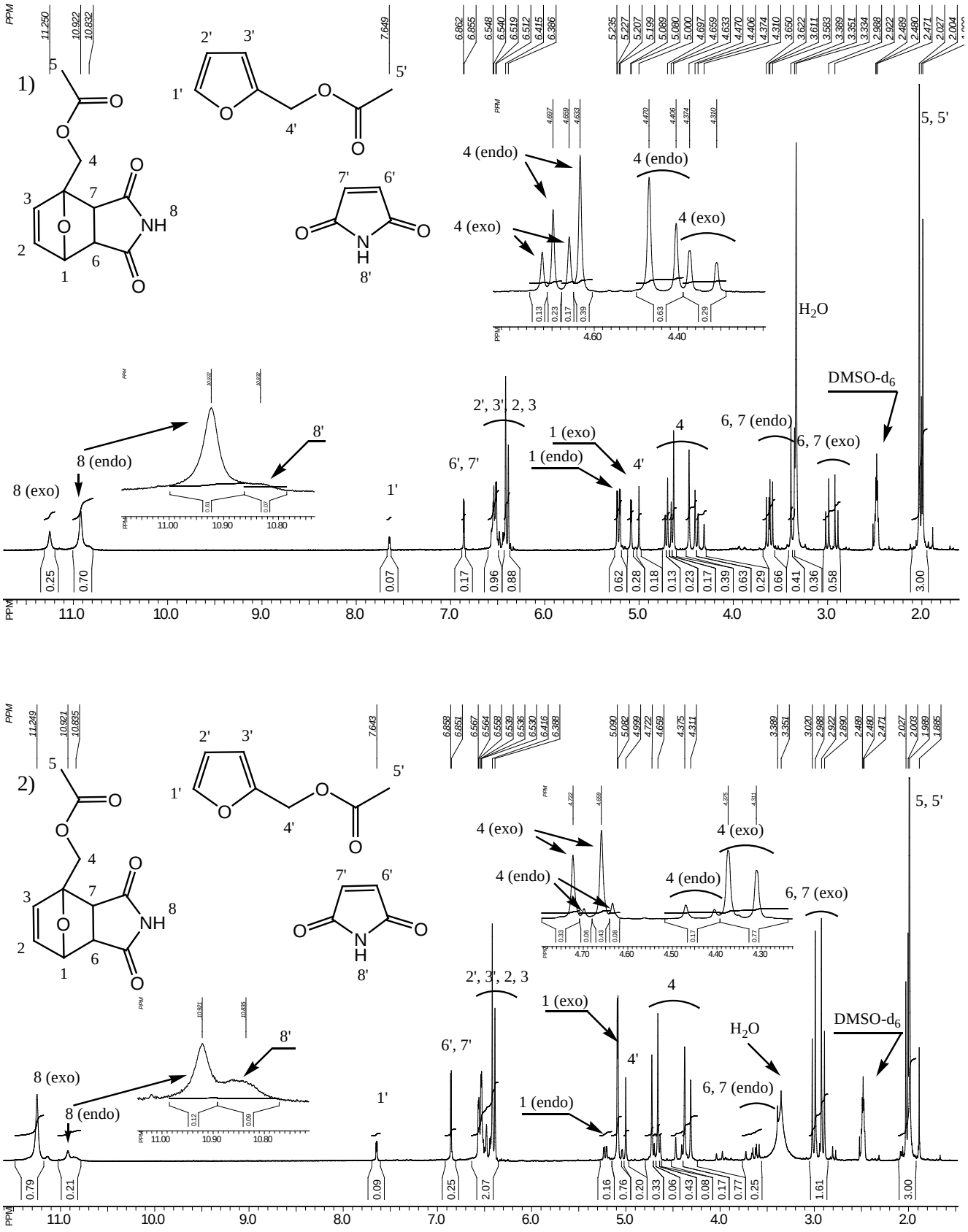

Figure 3. The PMR spectra of D-A adducts synthesized on the basis of FA and MI: **1**)at 20ºC; **2**) at 90ºC

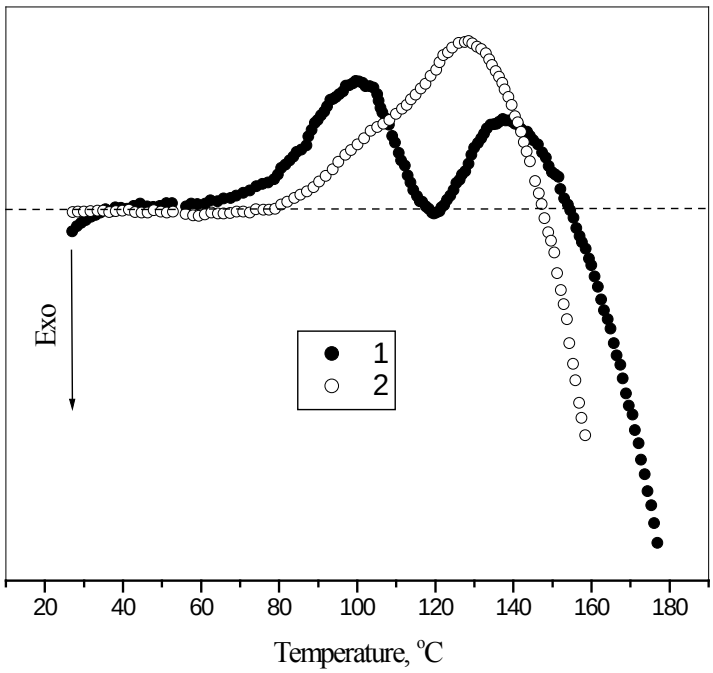

Figure 4. Thermograms of the decay of D-A adducts based on FA and MI: **1**-adduct, synthesized at 20 ºC; **2**- adduct synthesized at 90ºC

DSC thermograms (Figure 4) also show that the retrodiene reaction of adducts with a large quantity of exoisomers is somewhat delayed, and the adduct decay begins at a temperature of 20ºC higher.

The obtained results are thus indicative of that the nature of the second thermal effect, which is observed during the studies of the D-A reaction using the DSC method for the nonisothermal experiment is related to the isomerization process of the D-A adduct (the endo-to-exoform conversion).

CONCLUSIONS

1. D-A adducts were obtained through the FA and MI interaction and their isomer compositions were studied using the methods of the PMR spectroscopy and differential scanning calorimetry (DSC).
2. Endo-to-exoisomer isomerization conditions with the thermal effect of 8.8KJ/mole for 52% of endoisomer have been studied.
3. The kinematic studies of the formation and decay of endo/exoisomers (D-A) allow for their dedicated use for the homo- and copolymerization reactions of vinyl monomers.

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